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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C11D 7/52, C11C 3/10 C07C 67/02, C23G 5/032, 5/06	A1	(11) International Publication Number: WO 92/22631 (43) International Publication Date: 23 December 1992 (23.12.92)
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(21) International Application Number: **PCT/AU92/00262**(22) International Filing Date: **5 June 1992 (05.06.92)**(30) Priority data:
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601 St. Kilda Road, Melbourne, VIC 3004 (AU).**(81) Designated States: **AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), MG, NL (European patent), NO, SE (European patent), US.****Published***With international search report.*(54) Title: **DEGREASER COMPOSITION COMPRISING MONOUNSATURATED WAX ESTER**

(57) Abstract

A degreaser composition comprises an oil comprising a substantially paraffinic monounsaturated wax ester and an emulsifier or an emulsifier blend. The preferred oil is a fish oil extracted from Orange Roughy and Dory that has been treated in a transesterification process. The transesterification process comprises mixing the fish oil, an alcohol and an acid catalyst, and heating the mixture at a temperature between 40 and 150 °C for a prescribed time.

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- 1 -

DEGREASER COMPOSITION COMPRISING MONOUNSATURATED WAX ESTER

The present invention relates to a de-greaser composition and to a process for producing a component of the de-greaser composition from a fish oil.

De-greaser compositions are used widely in industry in applications such as, special cleaners for the maritime industry, cleaners for food processing equipment, and general and all purpose cleaners, and usually comprise an emulsifier/detergent and a hydrophobic solvent which carries the emulsifier into the grease.

There is an increasing recognition that, in addition to grease-removal and corrosion inhibition properties, de-greaser compositions should have other properties such

- 2 -

as biodegradability, non-toxicity and non-flammability.

An object of the present invention is to provide a de-greaser composition which exhibits the combination of properties described in the preceding paragraph.

5 Another object of the present invention is to provide a process for producing a component of the de-greaser composition from fish oil.

According to the present invention there is provided a de-greaser composition comprising:

- 10 (a) an oil comprising a substantially paraffinic monounsaturated wax ester; and
- (b) an emulsifier or an emulsifier blend.

It is preferred that the oil contains no or at most a low concentration of polyunsaturated fatty alcohols or acids as these are potential sites for the development of rancidity. It is particularly preferred that the oil contains less than 10% of polyunsaturated fatty alcohols or acids. It is more particularly preferred that the oil contains less than 5% of polyunsaturated fatty alcohols or acids.

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It is preferred that the oil comprises fish oil extracted from marine, more preferably deep sea marine, species. Typically, the fish oil is extracted from Orange Roughy (*Hoplostethus atlanticus*) and Dory. It is preferred that the fish oil is chemically modified by trans sterification to lower the pour point of the fish oil.

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- 3 -

It is preferred that the emulsifier or the emulsifier blend has a hydrophilic/lipophilic balance of between 5 and 9.

It is preferred that the emulsifier or the emulsifier blend is biodegradable as determined by AS 1792-1976.

It is preferred that the emulsifier or the emulsifier blend is non-toxic.

The emulsifier or the emulsifier blend may be formed in situ, eg, by reaction of polyethylene glycol and the oil to form polyethylene glycol esters or neutralization with an alkali of any free fatty acids to form soaps.

Typically, the emulsifier or emulsifier blend comprises one or more of polyethylene glycol 200 mono oleate, polyethylene glycol 400 dioleate, and laurylpolyethylene glycol ether 3 mole.

It is preferred that the de-greaser composition comprises 3% to 25%, more preferably 8% to 20%, of the emulsifier or emulsifier blend.

It has been found that at concentrations of less than 3% the emulsifier or emulsifier blend level is insufficient to impart rinsability and de-greasing strength to the oil and that at concentrations of more than 25% the product has insufficient "break" to leave a film which is necessary to impart anticorrosive properties.

- 4 -

According to the present invention there is also provided a process for producing an oil comprising a substantially paraffinic monounsaturated wax ester by transesterification of a fish oil, the process comprising:

- (a) mixing the fish oil, an alcohol and an acid catalyst; and
- (b) heating the mixture of the fish oil, the alcohol and the catalyst at a temperature between 40 and 150°C for a prescribed time.

By appropriate selection of the temperature, time, and relative amounts of the fish oil, alcohol, and catalyst, the above process produces a product which comprises a mixture of wax acid esters of the added alcohol, wax alcohols and residual wax esters and which has a lower pour point than the fish oil.

It is preferred that in step (a) the amount of the alcohol is between 0.2 and 20 times the amount of the fish oil on a molar basis.

It is preferred that the alcohol comprises one or more of methanol, ethanol, n-propanol, iso-propanol, ethylene glycol, propylene glycol, and isomers or butanol.

It is preferred that in step (a) the amount of the catalyst is between 0.2 and 5.0% of the total mass of the fish oil, the alcohol and the catalyst.

It is particularly preferred that the acid catalyst is an alkyl or arylalkylsulphonate.

- 5 -

The present invention is described further in the following examples.

Example 1 - Production of Transesterified Fish Oil

600 kg of Orange Rouphy oil, 450 l of ethanol and 10 kg of dodecylbenzenesulphonic acid were heated to 70°C and stirred at that temperature for 8 hours at which point equilibration was achieved. Upon cooling and evaporation of unconsumed ethanol, the resultant product was found to comprise 50% fatty acid ethyl esters, 40% free fatty alcohols and 10% unmodified wax esters and had a pour point of -6°C.

A complete analysis of the product is set out in Table 1 below.

Table 1

15	<u>Saturated</u>	<u>Ethyl Ester %</u>	<u>Alcohol %</u>	<u>Wax %</u>
	C 14	1.0	2.1	
	C 16	0.9	5.1	
	C 18	Tr	6.0	
	<u>Unsaturated</u>			
20	C 14-15	Tr	Tr	
	C-16:1	4.1	3.2	
	C-17	Tr	Tr	
	C-18:1	26.0	14.0	
	C-20:1	8.1	7.0	
25	C-22:1	3.1	5.6	

- 6 -

	C-24:1	Tr	1.9
	C-32		Tr
	C-33		2.1
	C-36		3.2
5	C-38		4.3
	C-40		3.7
	C-42		1.2
	C-42		Tr

Example 2 - Production of Transesterified Fish Oil

- 10 300 kg of Orange Rounphy oil, 440 l of isopropyl
alcohol and 5 kg of toluenesulphonic acid were heated to
85°C within 1 hour, maintained at that temperature for 10
hours, and then cooled. After unreacted isopropyl
alcohol was removed the resultant product was found to
15 comprise 48% fatty acid isopropyl esters, 37% free fatty
alcohols and 15% wax esters.

Example 3 - Production of Transesterified Fish Oil

- 1,000 kg of Dory oil, 110 l of methanol and 20 kg of
laurylsulphonic acid were heated to the reflux
20 temperature of the mixture (78°C) over 2 hours and
maintained at that temperature for 5 hours. After
evaporative removal of residual methanol, the resultant
product comprised 39% fatty acid methyl esters, 28%
fatty alcohols, and 28% unmodified wax esters and had a
25 pour point of 1°C.

- 7 -

Example 4 - Performance Characteristics of De-greaser Composition

5 A series of experiments was carried out to evaluate the biodegradability, toxicity, flammability, grease removal and corrosion inhibition properties of preferred de-greaser compositions of the present invention. The formulations of the de-greaser compositions tested in the experimental work are set out in Table 2 below.

Table 2

Formulation No.	Oil	Emulsifier	Comment
1.	Orange Roushy	Polyethyleneglycol	Product formulated with 3% emulsifier, ie at the lower limit of the scope of the present invention
2.	Orange Roushy	Polyethyleneglycol 200 monooleate	Product formulated with 10% emulsifier, ie within the scope of the present invention
3.	Orange Roushy	Polyethyleneglycol 200 monooleate	Product formulated with 15% emulsifier, ie within the scope of the present invention
4.	Orange Roushy transesterified as per Example 1	Polyethyleneglycol 400 dioleate	Product formulated with 15% emulsifier, ie within the scope of the present invention
5.	Dory oil	Polyethyleneglycol 200 monooleate	Product formulated with 80% emulsifier, ie at the upper limit of the present invention
6.	Orange Roushy	Polyethyleneglycol 200 monooleate	Product formulated with 25% emulsifier, ie outside the scope of the present invention

SUBSTITUTE SHEET

Known kerosine based
de-greaser

Known chlorinated
solvent
de-greaser

7. Kerosine 92%
Coconutdiethanolamide 4%
Laurylpolyethyleneglycol
ether 4 mole 4%

8. Methylene Chloride 65%
Butyl Icinol
Nonolyphenolethoxalate
5 mole 8 %
C 17 polyethyleneglycol
ether 3 mole 7%

SUBSTITUTE SHEET

- 10 -

As is evident from Table 2, formulations 2, 3, 4 and 5 comprise fish oil and emulsifier in proportions within the scope of the present invention; formulations 1 and 6 comprise fish oil and emulsifier in proportions at the limits of the scope of the present invention; and formulations 7 and 8 comprise commercially available preparations.

A brief discussion of the experimental work carried out on the formulations and the results is set out below.

10 (a) Biodegradability

The formulations were tested to ISO 7827 using the following standards: Soft Anionic - dodecylbenzene sulphonate; Soft Nonionic - nonylphenol ethoxalate. It was found that formulations 1 to 6 completely degraded within 10 days.

(b) Toxicity

Formulations 1 to 6 were non-toxic and formulations 7 and 8 were toxic.

(c) Flammability

20 Formulations 1 to 6 had a high flash point and were relatively non-flammable compared with formulation 7. Formulation 8 was non-flammable.

(d) Grease Removal and Corrosion Inhibition

25 A uniform coating of 2 mm grease was applied to 10 by 15 cm plates of mild steel, and the plates were subsequently treated as follows:

- 11 -

- (1) the plates were sprayed with unit volumes of the formulations,
- (2) the formulations were allowed to penetrate for 30 min,
- 5 (3) the plates were rinsed with cold water,
- (4) after a visual assessment of complete degreasing the plates were immersed in 5% hydrochloric acid to accelerate corrosion, and
- 10 (5) an assessment was made of the degree of corrosion after 2 hours.

The results are summarised in Table 3.

Table 3

	<u>Formulation</u>	<u>Degreasing</u>	<u>Corrosion</u>
	(1)	Ineffective	Not tested
15	(2)	Effective	Not evident
	(3)	Effective	Not evident
	(4)	Effective	Not evident
	(5)	Effective	Not evident
	(6)	Effective	Slight
20	(7)	Effective	Severe
	(8)	Effective	Severe

The results indicate that formulation 1 was an ineffective de-greaser, formulations 2 to 8 were

- 12 -

effective de-greasers, formulations 2 to 5 imparted significant corrosion inhibition, and formulation 4 imparted reasonable corrosion inhibition.

In summary, the experimental work established that formulations 2 to 6 in accordance with the present invention have a superior combination of biodegradability, non-toxicity, non-flammability, grease removal and corrosion resistance properties than the other formulations including formulations 7 and 8 of commercially available de-greaser compositions.

- 13 -

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A de-greaser composition comprising:
 - (a) an oil comprising a substantially paraffinic monounsaturated wax ester; and
 - (b) an emulsifier or an emulsifier blend.
2. The composition defined in claim 1, wherein the oil contains no or at most a low concentration of polyunsaturated fatty alcohols or acids.
3. The composition defined in claim 2, wherein the oil contains less than 10% of polyunsaturated fatty alcohols or acids.
4. The composition defined in claim 3, wherein the oil contains less than 5% of polyunsaturated fatty alcohols or acids.
5. The composition defined in any one of the preceding claims, wherein the oil comprises fish oil extracted from marine species.
6. The composition defined in claim 5, wherein the fish oil is extracted from Orange Roughy (*Hoplostethus atlanticus*) and Dory.
7. The composition defined in claim 5 or claim 6, wherein the fish oil is chemically modified by

- 14 -

transesterification to lower the pour point of the fish oil.

8. The composition defined in any one of the preceding claims, wherein the emulsifier or the emulsifier blend has a hydrophilic/lipophilic balance of between 5 and 9.

9. The composition defined in claim 8, wherein the emulsifier or the emulsifier blend is biodegradable as determined by AS 1792-1976.

10. The composition defined in any one of the preceding claims, wherein the emulsifier or the emulsifier blend is non-toxic.

11. The composition defined in any one of the preceding claims, wherein the emulsifier or the emulsifier blend is formed in situ.

12. The composition defined in any one of the preceding claims, wherein the emulsifier or emulsifier blend comprises one or more of polyethylene glycol 200 mono oleate, polyethylene glycol 400 dioleate, and
5 laurylpolyethylene glycol ether 3 mole.

13. The composition defined in any one of the preceding claims, comprising 3% to 25% of the emulsifier or emulsifier blend.

14. The composition defined in claim 13, comprising 8 to 20% of the emulsifier or emulsifier blend.

- 15 -

15. A process for producing an oil comprising a substantially paraffinic monounsaturated wax ester by transesterification of a fish oil, the process comprising:

- 5
- (a) mixing the fish oil, an alcohol and an acid catalyst; and
 - (b) heating the mixture of the fish oil, the alcohol and the catalyst at a temperature between 40 and 150°C for a prescribed time.

16. The process defined in claim 15, wherein the amount of the alcohol is between 0.2 and 20 times the amount of the fish oil on a molar basis.

17. The process defined in claim 15 or claim 16, wherein the alcohol comprises one or more of methanol, ethanol, n-propanol, iso-propanol, ethylene glycol, propylene glycol, and isomers or butanol.

18. The process defined in any one of claims 15 to 17, wherein the amount of the catalyst is between 0.2 and 5.0% of the total mass of the fish oil, the alcohol and the catalyst.

19. The process defined in any one of claims 15 to 18, wherein the acid catalyst is an alkyl or arylalkylsulphonate.

- 16 -

20. A transesterified fish oil produced by the process of any one of claims 15 to 19.

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent classification (IPC) or to both National Classification and IPC
Int. Cl.⁸ C11D 7/52; C11C 3/10; C07C 67/02; C23G 5/032, 5/06

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System

Classification Symbols

IPC

C11D 7/52; C11C 3/10

Documentation Searched other than Minimum Documentation
to the extent that such Documents are included in the Fields Searched⁸

AU:IPC as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category [*]	Citation of Document, ¹¹ with indication, where appropriate of the relevant passages ¹²	Relevant to Claim No ¹³
X	AU,A, 44045/89 (AARHUS OLIEFABRIK A/S) 5 APRIL 1990 (05.04.90) page 3 lines 1-8, 30-34; page 4 lines 25-33; page 5 lines 6-17; page 6 lines 20-27; page 8 line 21.	1-4, 12-14
X	AU,B, 63413/65 (292780)(CHAS. PFIZER & CO. INC.) 2 MARCH 1967 (02.03.67). Example XI.	1-4, 12-14
X	AU,B, 22526/56 (217587)(Louis McDonald) 18 APRIL 1957 (18.04.57) Page 19.	1-5
(continued)		

Special categories of cited documents:¹⁰

- "A" Document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search
7 August 1992

Date of Mailing of this International Search Report

18 Aug 1992 (18.08.92)

International Searching Authority

AUSTRALIAN PATENT OFFICE

Signature of Authorized Officer

J. BODEGRAVEN

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

X	EP,A, 0292846 (INNOVA DI RIDOLFI FLORA &C.S.a.S.) 30 November 1988 (30.11.88). Page 3 lines 55-58.	15
X	GB,A, 587533 (COLGATE-PALMOLIVE-PEET COMPANY) 29 May 1947 (29.05.47) Page 1 lines 70-102; Page 2 lines 21-22, 123-128.	15

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

- ☐ Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:
- ☐ Claim numbers ..., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
- ☐ Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4a

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

- ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
- ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
- ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

[illegible]

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 92/00262

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member		
AU	44045/89	DK	5331/88	EP 435943
		ES	2024080	
		WO	9003419	
		DK	542/91	
		FI	911436	
		NO	901003	
EP	292846	IT	8720700	JP 1070439
		US	5130061	